EXPERIMENTAL RELEASES OF LIQUID HYDROGEN[†]

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If the hydrogen economy is to progress, more hydrogen fuelling stations are required. In the short term, in the absence of a hydrogen distribution network, the most likely means of supplying the fuelling stations will be by liquid hydrogen road tanker. The development will clearly increase the number of tanker offloading operations significantly and these may need to be performed in more challenging environments with close proximity to the general public.

The work described in this paper was commissioned in order to determine the hazards associated with liquid hydrogen spills onto the ground at rates typical for a tanker hose failure during offloading.

Experiments were performed to investigate spills of liquid hydrogen at a rate of 60 litres per minute. Measurements were made on unignited and ignited releases. These included:

- Concentration of hydrogen in air, thermal gradient in the concrete substrate, liquid pool formation, temperatures within the pool
- Flame velocity within the cloud, thermal radiation, IR and visible spectrum video records
- Sound pressure measurements
- An estimation of the extent of the flammable cloud was made from visual observation, video, IR camera footage and the use of a variable position ignition source

KEYWORDS: LH2, Flame speed, Thermal radiation, Hydrogen concentration, Flammable cloud, Liquid pool, Explosion

1. INTRODUCTION

Cryogenic liquid storage and transfer has been safely executed for many years in secure and regulated industrial sites. However its use in relatively congested, highly populated urban areas presents a new set of problems in relation to security, safety and associated planning. Research is needed to identify and address safety issues relating to bulk liquid hydrogen storage and transfer facilities associated with hydrogen refuelling stations located in urban environments.

Liquid hydrogen has significantly different properties to other more common cryogenic gases, as can be seen from the values presented in Table 1.

It can be seen from these properties that attempting to simulate the release behaviour of liquid hydrogen based on other more easily handled cryogens is unlikely to yield useful results. The liquid phase has very low density compared to the other industrial cryogenic liquids and the vapour phase at the boiling temperature is only just negatively buoyant in ambient air (air density approximately $1.2\ \mathrm{kg/m^3}$)(1). Furthermore, a release of liquid hydrogen can result in significant cooling of the surroundings causing condensation of nitrogen and oxygen from the air and even the freezing of these gases to produce a solid.

In addition, the general combustion properties, such as flame speed and ignition behaviour, for a cool, dense vapour cloud of hydrogen with high proportions of condensed water present are unknown and therefore need to be studied.

This paper gives an overview of experimental work to investigate the behaviour of liquid hydrogen released to atmosphere in both un-ignited and ignited scenarios.

2. EXPERIMENTAL AIMS

A number of distinct areas of spill behaviour were investigated:

- Hydrogen dispersion from unignited spills
- On ground liquid spill formation
- Spills into free air
- Spill behaviour with respect to specific storage conditions
- Flame speed and extent from ignited spills
- Thermal radiation from ignited spills
- Sound pressure level measurement from ignited hydrogen clouds.

All the releases made were chosen to replicate a reasonably foreseeable release from the failure of a transfer hose coupling during LH2 transfer. Catastrophic failure of the containment vessel was not investigated as it is considered to be a much less likely event.

Table 1. Properties of liquid hydrogen and other common cryogenic gases[1]

	Hydrogen	Nitrogen	Oxygen	Methane
Liquid density (kg/m^3)	70.8[2]	804	1142	424
Gas density at boiling point (kg/m^3)	1.34[2]	4.61	4.48	1.80
Boiling point (K)	20.28	77.35	90.18	109.15
Freezing point (K)	14.01	63.29	54.75	90.67

[1] CRC Handbook of Chemistry and Physics, 58th Ed.

[2] NASA document NSS 1740.16 : "Hydrogen and Hydrogen Systems, Guidelines for Hydrogen System Design, Materials Selection, Operations, Storage and Transportation".

3. EXPERIMENTAL RELEASES

All the releases in this work were made from hydrogen stored in a road tanker provided by BOC UK. The liquid hydrogen was piped from the tanker to the release point through a 25 mm diameter vacuum insulated flexible line. Most of the releases were made from a nominal storage pressure of 1bar(g) which gave a nominal release rate of 60 litres per minute of liquid hydrogen. A schematic of the release system is shown in Figure 1 and a photograph of the test area with tanker and pipe-work in Figures 2 and 3. The release system comprised the liquid hydrogen tanker, 20 metres of 25 mm bore vacuum insulated hose, a release valve station with bypass, purge and release valves and a 6 m high vent stack to vent excess hydrogen. The tanker contains up to 2.5 tonnes of hydrogen in a vacuum insulated internal tank surrounded by an outer jacket containing liquid nitrogen. The tanker is equipped with vent valves such that the pressure within the tanker can be lowered. It is also fitted with a liquid hydrogen/air heat exchanger such that the pressure in the tanker can be raised. To raise the pressure within the tanker LH2 is allowed to flow into the heat exchanger where it vaporises; this vapour is then fed into the vapour space in the tanker in order to pressurise the liquid hydrogen. The tanker is fitted with a bursting disc rated at 12 bar to protect against over-pressurisation. The storage conditions of the liquid hydrogen are important if consistent results are to be obtained. As the pressure of hydrogen delivered in the tanker was up to 5 bar, the vapour space of the tanker was depressurised and then the pressure in the tanker was raised to approximately 1 bar before each series of releases. This was carried out in order to achieve consistency and to obtain a liquid spill without significant flash vaporisation.

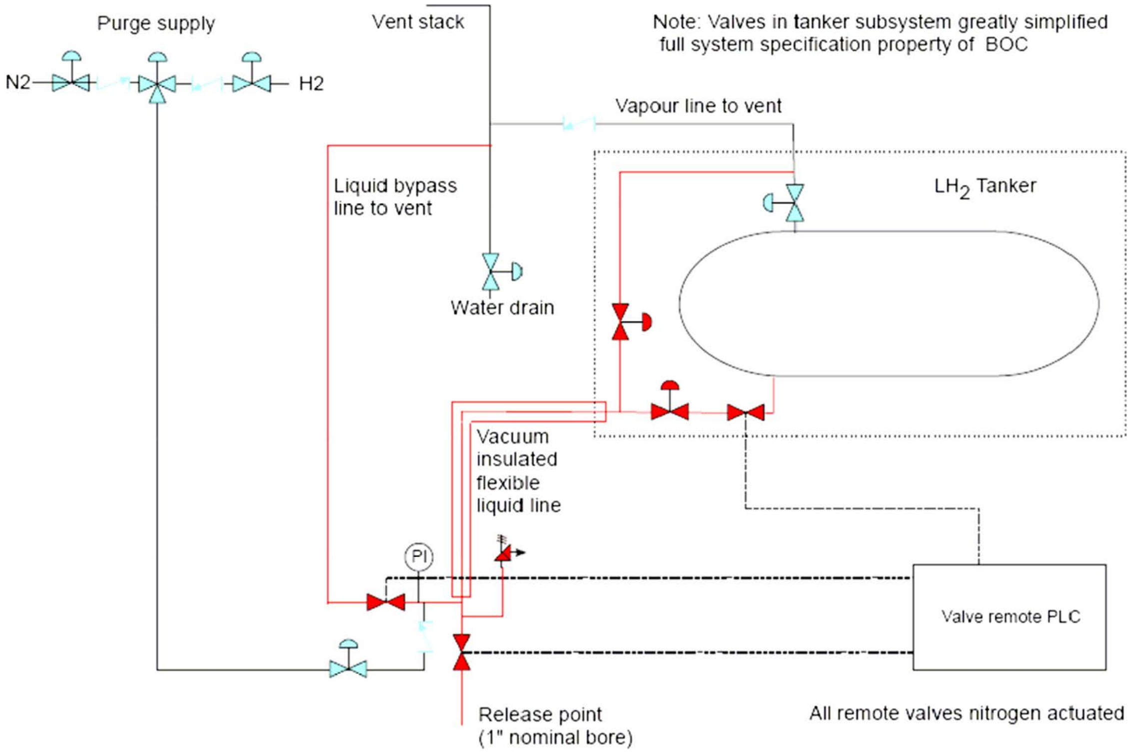

Figure 1. Schematic of release system

Figure 2. Test area and tanker

The releases were made onto or above a concrete surface. For unignited releases the following measurements were made:

- Storage pressure – the pressure in the tanker during the release, this remained constant, as the amount of liquid being withdrawn was small compared to the overall volume of the tanker
- Release pressure – this was the pressure measured just upstream of the final release valve
- Pool size – the extent of any pool of liquid formed on the ground; this was determined by a combination of video and thermocouple measurements – twenty four 1 mm type E thermocouples were deployed in contact with the ground (see Figure 4).
- Hydrogen concentration – this was determined from temperature measurements within the cloud using an adiabatic mixing assumption as described in work by others (Chirivella 1986); a total of thirty 1 mm type E thermocouples were deployed (see Figure 5).
- Pool temperature – the temperature of the hydrogen being released and that forming a pool on the ground was determined by thermocouple measurements

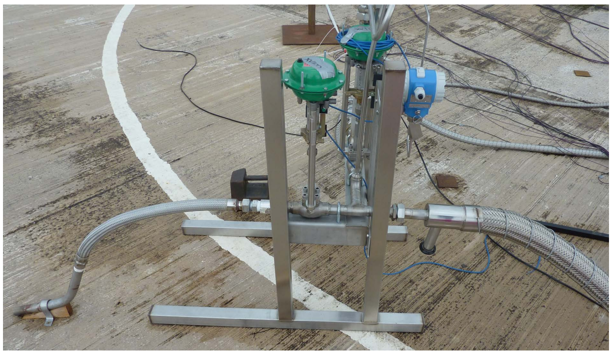

Figure 3. Release pipework

Figure 4. Pool thermocouples

- Substrate temperature – the temperature within the concrete pad in the vicinity of the release was measured with three thermocouples embedded in the concrete at depths of 10,20 and 30 mm
- Meteorological measurements – including wind-speed, wind direction, air temperature and humidity were determined at release height and 2.5 metres above the ground at the edge of the release area.

For ignited releases additional measurements were made of:

- Flame speed – by high speed video recording and thermal imaging
- Thermal radiation – using Medtherm fast response ellipsoidal radiometers (see Figure 6)
- Pressure – using Kulite pressure transducers
- Sound measurement.

4. TEST PROGRAMME

The work plan involved releases of liquid hydrogen at a nominal rate of 60 litres per minute for different durations and different orientations. For all of the tests the liquid

Figure 5. Concentration measurements

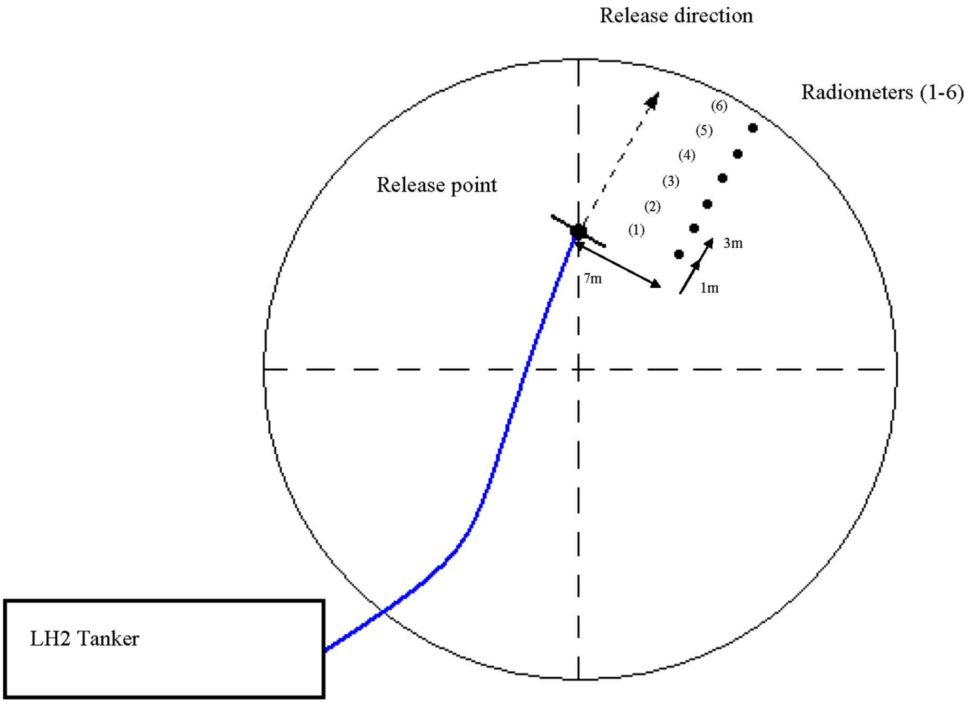

Figure 6. Radiometer positions on test pad

hydrogen was released through a 1inch nominal bore Schedule 40 pipe, which gave an internal diameter at the orifice of 26.3 mm.

A number of tests were performed in which LH2 was released in one of the following ways; a) horizontally along the ground, b) vertically downwards from 100 mm above the ground, c) horizontally at a height of 860 mm above the ground. The nominal storage pressure was 1 bar and the nominal release pressure was 0.2 bar for all the releases reported here.

5. RESULTS

5.1 UNIGNITED TESTS

The tests which impinged hydrogen onto the ground all produced a pool of liquid once the ground had cooled sufficiently, usually about 2 minutes into the release. In addition a large solid deposit, which had the appearance of snow, was produced. Both the liquid and the "snow" persisted for several minutes after the release ended.

The thermocouple measurements taken in contact with the ground during the release are shown in Figure 7. These show a degree of sub-cooling is occurring as the hydrogen is released and evaporates, with temperatures as low as 16 K being recorded. In addition steps are evident in the temperature traces as the temperature increases after the release has ended. This is indicative of the melting and boiling of the condensed air.

The temperatures typically recorded in the concrete layer underneath the release point are shown in Figure 8 at depths of 10, 20 and 30 mm.

The cloud of hydrogen vapour is visible during the release due to condensation of water within the cloud. A photograph showing a typical hydrogen cloud formed by a release is shown in Figure 9.

A concentration contour graph is shown in Figure 10 representing a snapshot of experimental data from a typical horizontal release at ground level. The graph was generated using measured hydrogen concentration data at various heights and distances from the release point. The red line represents the 4% concentration contour (LFL) and the green line the 30% concentration contour (stoichiometric). The graph gives an estimate of hydrogen concentrations at a specific time during the release when the wind direction was such that the hydrogen cloud passed through the sensors.

A photograph of the pool of liquid produced during a release is shown at Figure 11. A solid deposit can also be seen close to the release point. A close up photograph of the solid deposit can be seen in Figure 12.

This solid persisted for some time after the release appearing to co-exist with a boiling pool of liquid. The solid deposit appeared to sublime rather than melt, possibly due to the relatively close melting and boiling points compared to ambient temperature.

After one of the tests an attempt was made to ignite the vapour above the solid deposit. The deposit ignited and a vigorous flame ensued, but no explosion occurred.

Initial thoughts are that the solid deposit is a mixture of solid nitrogen and oxygen with some liquid hydrogen trapped within the matrix similar to that observed when butane forms hydrates with water (Allen 2000).

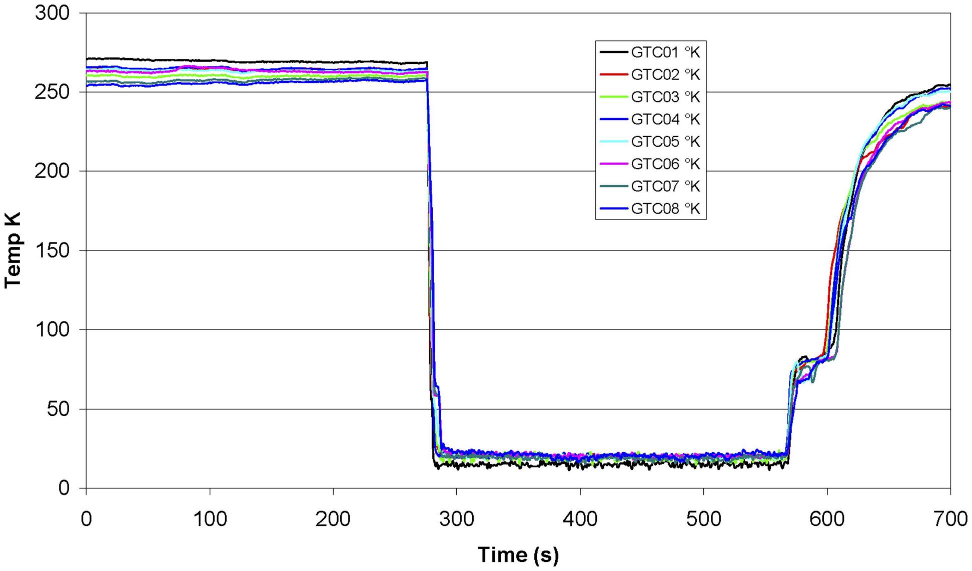

Figure 7. Surface concrete temperatures for the first eight sensors during the release

5.2 IGNITED RELEASES

A number of ignited releases were performed with varying parameters. The release rate and pressure were the same as for the unignited releases. All the ignited releases performed to date have been made with the hydrogen released horizontally along the ground at ground level. A number of releases were made at night to enable the flame to be more easily visualised. It should be noted that the clouds of hydrogen produced by the release of liquid hydrogen could occasionally be difficult to ignite; on one occasion four pyrotechnic igniters were fired within the cloud with no resulting ignition of the hydrogen gas. The reason for this is not clear, although it may be that the gas cloud was over-rich in hydrogen at the point that the igniters were fired.

5.2.1 Typical Burning Behaviour

The first ignited release (see Figure 13) was performed with the ignition timed immediately after the release had stabilised and before any pool or solid had accumulated on the

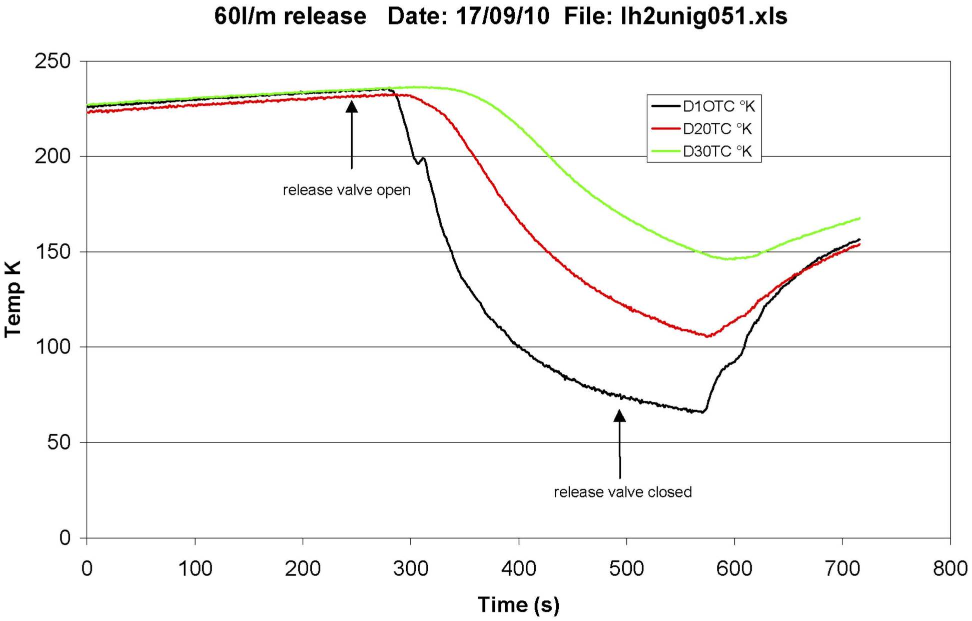

Figure 8. Concrete temperatures during the release

Figure 9. Hydrogen cloud

ground. On ignition there was a soft report followed by a low rumble and then a gentle jet flame as the hydrogen issuing from the release pipe burned. The ignition was approximately 9 m from the release point and at 1 metre high. The flame speed was measured from the high speed video and found to develop up to 30 m/s.

A typical radiometer trace for one of the ignited releases is shown in Figure 14, showing an initial peak due to the burning back of the cloud and then a steady state burning of the LH2 as it is fed into the existing fire.

The fraction of potential heat release that is emitted in the form of radiation is referred to as the radiative fraction, ξ, and is defined in Equation (1).

$$Q_r = \xi M \Delta H_c \tag{1}$$

where :

Q_r = Heat radiated (kW)
ξ = Radiative fraction (between 0 and 1)
M = Mass rate of fuel combustion (kg/s)
ΔH_c = Heat of combustion of the fuel (kW/kg)

The radiative fraction depends upon the fuel type and whether contaminants are present within the burning cloud. Hydrogen flames typically radiate less than flames from the combustion of hydrocarbon gases. The radiative fraction was estimated for the steady burning periods of the LH2 release experiments, that is when the initial cloud had burned back and the hydrogen was being consumed as it was released and evaporated.

It is common to approximate the radiative fraction of a flame based on radiometer readings taken at a significant distance from the flame such that an inverse square law can be reasonably applied. However, in this case the flame was elongated along the line of the radiometers and was generally close to the ground. It can be seen that the readings of the first three radiometers are very similar to each other. This is as would be expected from the flame shape observed on the video recordings. For this reason, a semi-cylindrical radiating heat source was assumed for the purposes of estimating the radiative fraction and the total radiated heat estimated using Equation (2).

$$Q_r = (1 + \alpha)\pi \, d \, L \, q_r \tag{2}$$

where :

Q_r = Heat radiated (kW)
d = Distance to radiometer (m)
L = Length of flame (m)
q_r = Heat flux at radiometer (kW/m^2)
α = Reflection coefficient of concrete surface below the flame

Data from two of the ignited releases was analysed in this way, assuming a reflection coefficient for the concrete between the extremes of 0 and 1, and the radiative fraction was estimated as being between 0.06 and 0.12. This estimate compares reasonably well with previously reported values

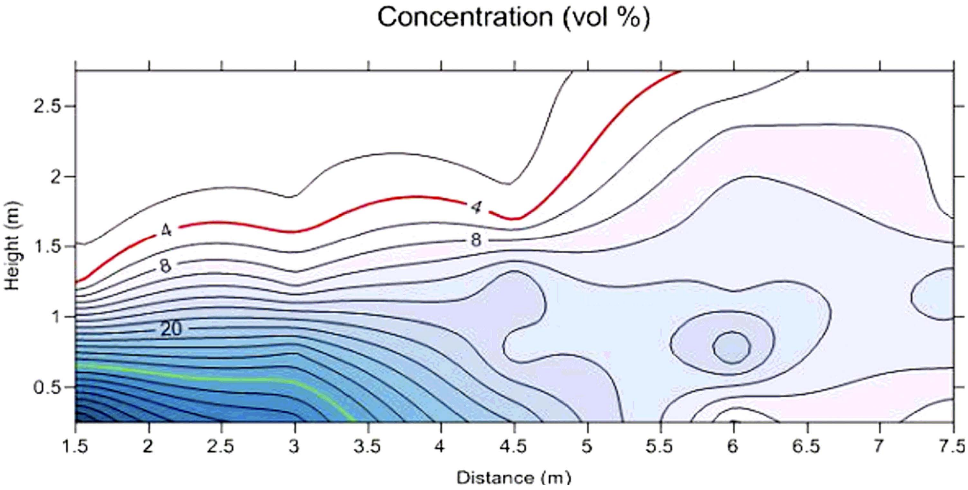

Figure 10. Concentration contour graph

Figure 11. Pool and solid

Figure 13. Ignited cloud

for gaseous and LH2 hydrogen releases (Studer 2009, Friedrich 2011).

5.2.2 Explosion

In one experiment there was evidence of an explosion occurring close to the release point after LH2 had been released at ground level, during windy conditions, for about 4.5 minutes. The explosion occurred after the hydrogen cloud had been ignited, burned back to the release point and then burned steadily for about 4 seconds. The radiometer trace from this experiment is shown in Figure 15; the second peak, corresponding to the explosion, is evident.

Several attempts were made to reproduce the phenomenon without success, although the conditions on those occasions were far less windy than when the explosion had occurred. It is possible that oxygen enrichment of the condensed air may have occurred due to oxygen having a higher boiling temperature than nitrogen, and that this effect was more evident during the windy conditions. It is postulated that the explosion was either a gas phase explosion resulting from a sudden release of oxygen from the solid due to a rapid phase change, or even a rapid reaction within the condensed slurry of solidified air and LH2 if the oxygen concentration were high enough (NASA, 1997).

Figure 12. Solid 3 minutes after release

The explosion was sufficiently energetic to be heard over a kilometre away. Unfortunately, at the time of the explosion no pressure measurements were being made. Therefore, it was necessary to estimate the “size” of the explosion by other means.

An estimate of the maximum size was made based on the failure of the explosion to break Perspex windows in a nearby storage building. On this basis, the TNT equivalent mass was estimated as less than 4 kg. At 100% equivalence this would equate to approximately 100 g of hydrogen, and so several hundreds of grams of hydrogen could be expected to be involved in a gas phase explosion of this magnitude.

Another estimate was made based on the radiometer response during the explosion (that is the area under the second peak represents the total energy per m^2 received at the radiometer). Since the resulting explosion almost engulfed the nearest radiometers, the estimate was based on the furthest radiometer and a hemispherical heat flux assumed. It was also assumed that the radiative fraction during the explosion was similar to that during steady burning. On this basis the quantity of hydrogen rapidly burned in the explosion was estimated as 400 to 1200 g, yielding approximately 100 MJ.

6. MAIN FINDINGS

The release of liquid hydrogen in contact with a concrete surface can give rise to pooling of liquid once the substrate is sufficiently cooled.

Release of liquid hydrogen in close proximity to a concrete surface can result in subcooling due to vapourisation.

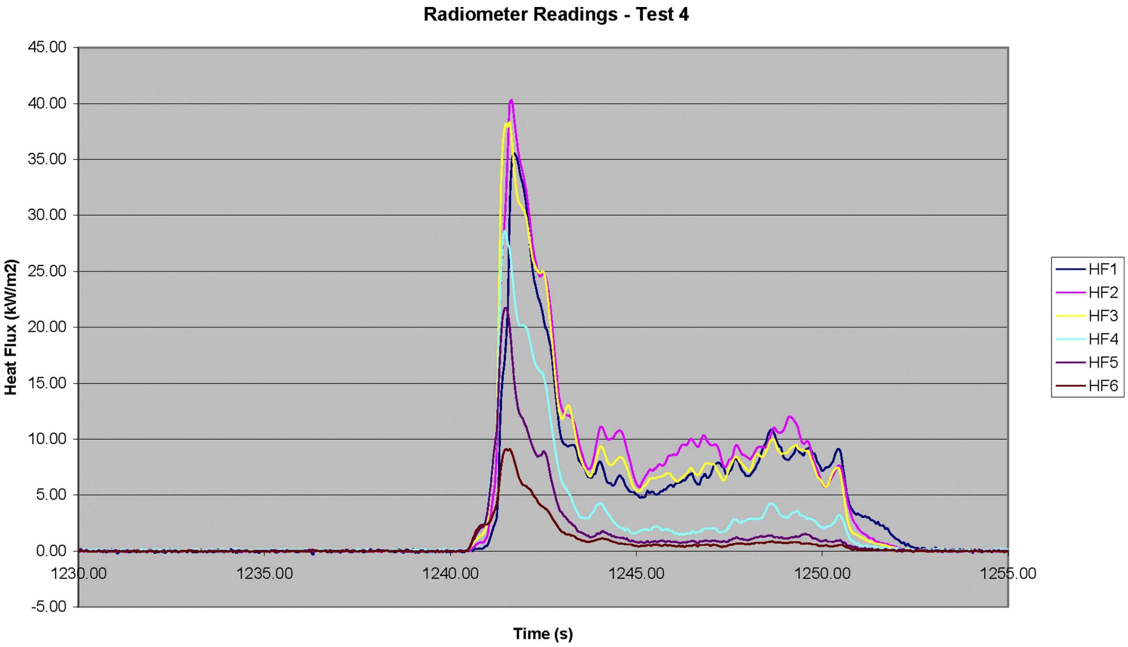

Figure 14. Typical radiometer trace from ignited release

The release of liquid hydrogen at a rate consistent with the failure of a 1 inch transfer line produces a flammable mixture at least nine metres downwind of the release point.

The release of hydrogen in contact with a concrete surface produces a solid deposit of oxygen and nitrogen once the substrate is sufficiently cooled.

The radiative fraction of ignited LH2 fires was estimated as being between 0.06 and 0.12.

After one prolonged LH2 release during windy conditions an explosion occurred some time after the initial gas cloud had ignited and burned back to the release point. It is thought that this occurred as a result of the sudden reaction of hydrogen with the air, possibly enriched with oxygen,

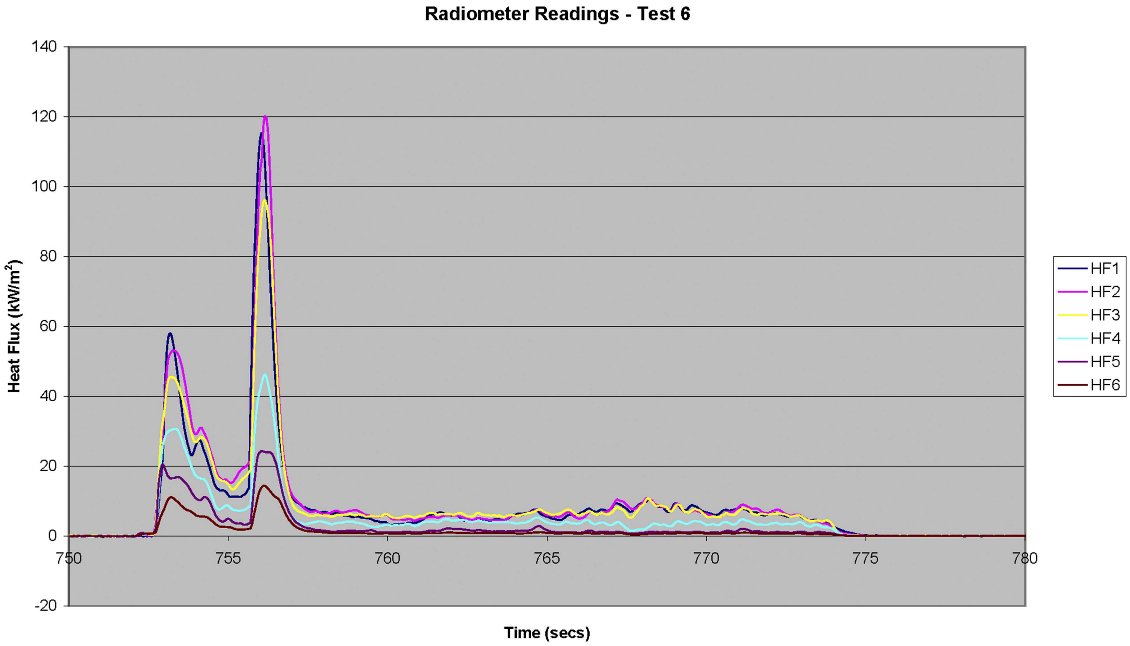

Figure 15. Radiometer trace from ignited release exhibiting an explosion

that was condensed on the ground. It is not clear whether the reaction took place in the gaseous or condensed phase.

The quantity of hydrogen involved in the explosion has been estimated at between 400 g and 1200 g (yielding approximately 100 MJ).

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